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TECHNICAL REPORT NO. 10

Vibrational Spectroscopy of the Electrode-Solution Interphase. III. Use of FTIR Spectroscopy for Observing Double Layer Reorganization.

By

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Results are presented for experiments designed to observe structural changes in the electrical double layer under different potential modulations. Results are presented for non-aqueous systems in this report.

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VIBRATIONAL SPECTROSCOPY OF THE ELECTRODE-SOLUTION INTERFACE.

III. USE OF FOURIER TRANSFORM SPECTROSCOPY FOR

OBSERVING DOUBLE LAYER REORGANIZATION

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ABSTRACT

Potential dependent Fourier transform infrared spectra recorded in situ at a polarized platinum electrode in acetonitrile solutions clearly show the interplay between adsorbed acetonitrile and preferentially adsorbed anions. Water in at least two forms is observed as independent structures in the system.

In situ infrared spectroscopy of the electrode-solution interface has recently been used to characterize a variety of electrochemical phenomena (1-6). Basically, three successful techniques exist for obtaining such spectra: (a) electromodulated specular reflectance (5), (b) Fourier transform infrared spectroscopy at differentially polarized surfaces (2), and (c) polarization modulation specular reflectance (6). In this paper, we look at the changes in the composite structure of the double and diffuse layers of a platinum electrode in acetonitrile solutions. It is shown that the technique is sensitive enough to observe the spectral differences in adsorbed and bulk acetonitrile, as well as the differences in the solution structure as anions are specifically adsorbed at potentials positive to the potential of zero charge. Absorbance changes due to water molecules associated with the anion and acetonitrile are also observed.

EXPERIMENTAL

Spectroscopy and Electrochemistry

Spectra were recorded on a Nicolet 7199 FTIR system. Potential step programs were provided by a HI-TEK Instrument DT2101 potentiostat and PPR1 waveform generator. The waveform generator was triggered by a TTL signal from the Nicolet computer denoting the beginning of data acquisition. For

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sequential potential steps, various delay time sequences were used to record spectra at the same times after the potential was changed so that signal averaging could be used to increase signal-to-noise ratio (7). The spectra herein are the difference between 40 averaged spectra at the sample and base potential. The base potential of −0.50 V vs Ag/Ag^+ (0.01 M in 0.1 M tetrabutylammonium tetrafluoroborate or lithium perchlorate in acetonitrile) reference was chosen because of its proximity to the pzc of platinum in the chosen electrolytes.(8)

Chemicals

Acetonitrile (Caledon, HPLC grade, 0.003% water) was distilled twice from calcium hydride, and stored before use in sealed containers over Woelm alumina (Super grade I). The cells were dried in a vacuum oven at 150°C before use, and dry argon admitted to the oven as the vacuum was released. Transfer of solvent/electrolyte to the cell was made in an argon filled glove bag. Electrolytes were purified (7) and dried similarly in a vacuum oven before use.

Cells, Mountings, and Electrodes

The description of the cell construction and the mountings for the Nicolet sample cavity has been described elsewhere (7). The electrode used was a platinum mirror that had been polished with 0.05 μm alumina and dried in a vacuum oven immediately before use. Solution thickness in the optical path was determined by use of the integrated extinction coefficient method as previously described (7).

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RESULTS

Differential spectra of a 0.10 M solution of tetrabutylammonium tetrafluoroborate in anhydrous acetonitrile as a function of applied potential are shown in Figure 1. The base potential of each spectrum is −0.50 V vs the Ag/Ag^{+} reference electrode. Peaks extending downward correspond to increased absorption of radiation at the sample potential (less absorbance at the base potential of −0.50 V). The converse is true for peaks extending upwards. Figure 2 shows the spectra from the same system after it is made 0.10 M in water. Most noticable are new absorbance changes in the region from about 3200 cm^{-1} to 3700 cm^{-1}, around 1650 cm^{-1}, and broadening in the band around 1070 cm^{-1}. Spectra from the same experiment performed on an anhydrous solution of 0.10 M lithium perchlorate are presented in Figure 3, and Figure 4 gives the corresponding spectra after addition of water, as in the tetrafluoroborate system. The solution thickness between the window and the electrode of 0.75 µm was the same in all four experiments.

The C≡N stretch region between 2200 cm^{-1} and 2400 cm^{-1} is observed to be blue shifted at potentials positive to the base potential in all cases. The perchlorate asymmetric stretch fundamental region (1102 cm^{-1}) is not shifted at positive sample potentials, but is broadened. Further broadening is noticed in the presence of water. The same is true of the tetrafluoroborate anion asymmetric stretch region (1060 cm^{-1}), and some fine structure appears on the band. Normal transmission spectra of perchlorate and tetrafluoroborate anion in acetonitrile show no fine structure in this region.

DISCUSSION

The spectra contain a considerable number of complex bands and clearly their interpretation will give detailed information on the changes in the

number and the nature of various species on the electrode surface and in the double layer. Certain aspects are readily explained: the increasing adsorption of acetonitrile with increasing positive potential beyond −0.5 V is clear from the progressively increasing intensity of the downward extending band at about 2350 cm^{-1} which is strongly blue shifted by the perturbation of the molecule due to adsorption (2) (bulk acetonitrile gives a −C≡N fundamental at 2220 cm^{-1}); the increasing amount of anion in the double layer is shown by the other dominant downward bands at 1102 cm^{-1} and 1060 cm^{-1} for perchlorate and tetrafluoroborate respectively. The upward extending fine structure on the −C≡N band between 200 cm^{-1} and 2400 cm^{-1} is due to decreased absorption by bulk acetonitrile.

The complex bands between 3300 cm^{-1} and 3600 cm^{-1} and also near 1600 cm^{-1} are particularly interesting and they can be ascribed to the stretching modes of water in different environments. The broad band at 3350 cm^{-1} corresponds to extensively hydrogen-bonded water, possibly associated with the anion, and increasing in intensity as more anions enter the double layer. The sharper bands of opposite sign near 3625 cm^{-1}, 3550 cm^{-1} and 1625 cm^{-1} probably arise from water which is less perturbed by hydrogen bonding. A very likely candidate is the symmetrically bonded complex between two acetonitrile molecules and one water molecule. This is a well characterized species for which the ν_3, ν_1 and ν_2 vibrational modes are at the frequencies given above (8-11). The intensities of these bands are seen to decrease as the potential is made more positive indicating a decreasing population of this complex.

These assignments lead to a simple explanation of the spectra in terms of the dependence on the electrode potential of the population of the various species in the optical path. As a consequence of making the electrode potential more positive there is an increased amount of adsorbed acetonitrile

and of anions in the double layer. Movement of anions into the double layer will not, however, deplete the thin layer of electrolyte solution in the optical path because [illegible]ration of the 0.1 M electrolyte solution will readily replenish the layer; thus there will be a net increase in the total number of anions in the IR beam and also of the water associated with them, as is shown by the spectra. As a result, some acetonitrile, both free and complexed with water, will be displaced from the fixed volume of the thin layer as is observed from changes in the acetonitrile bands and in the bands for complexed water, particularly at high potentials. These changes are summarized in Figure 5.

There are also contributions from the cation. A bipolar band is observed in the region 2900 - 3050 cm^{-1} corresponding to the C-H stretch of TBAF. The major part of the band is upward extending which corresponds to the decrease in the amount of the cation in the double layer with increasing positive potential. The small lobes of opposite sign indicate also that there are changes in the detailed band shape.

It is clear from the data presented here that the method employed will be of great value in probing changes in the structure of the electrical double layer.

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FIGURE LEGENDS

(1) Differential reflectance FTIR spectra of 0.10 M tetrabutylammonium tetrafluoroborate in anhydrous acetonitrile. Solution thickness = 0.75 microns. Spectra recorded under steady state conditions at each indicated potential. Spectrum at the −0.50 V base potential was always subtracted from those obtained at the other potential.

(2) Same as Figure 1 except water concentration 0.10 M.

(3) Differential reflectance FTIR spectra of 0.10 M lithium perchlorate in anhydrous acetonitrile. For other notes, see Figure 1.

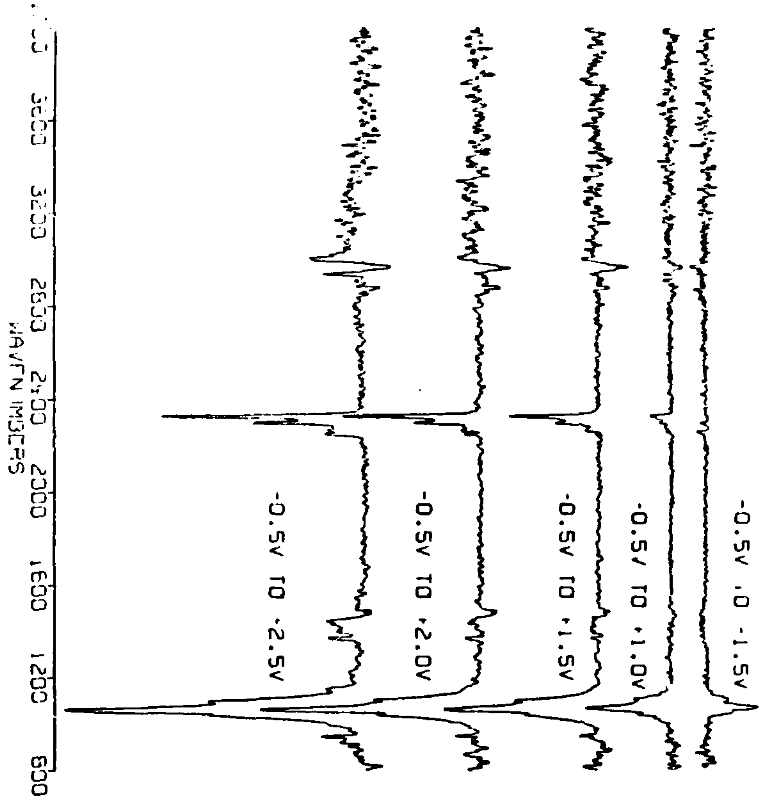
(4) Same as Figure 3 except water concentration 0.10 M.

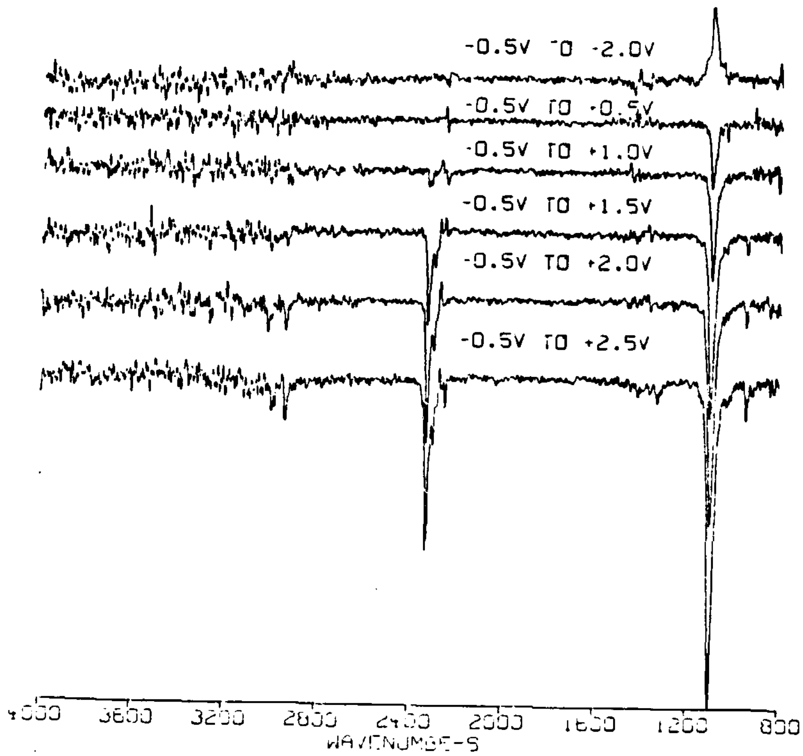
(5) Model [illegible] account for spectral observations.

[illegible]

[illegible]

Movement of species onto or off the electrode surface and into or out of the thin electrolyte layer caused by the potential step from the more positive potential to the more negative potential is represented by the arrow labelled b. The arrow labelled f represents the reverse process.

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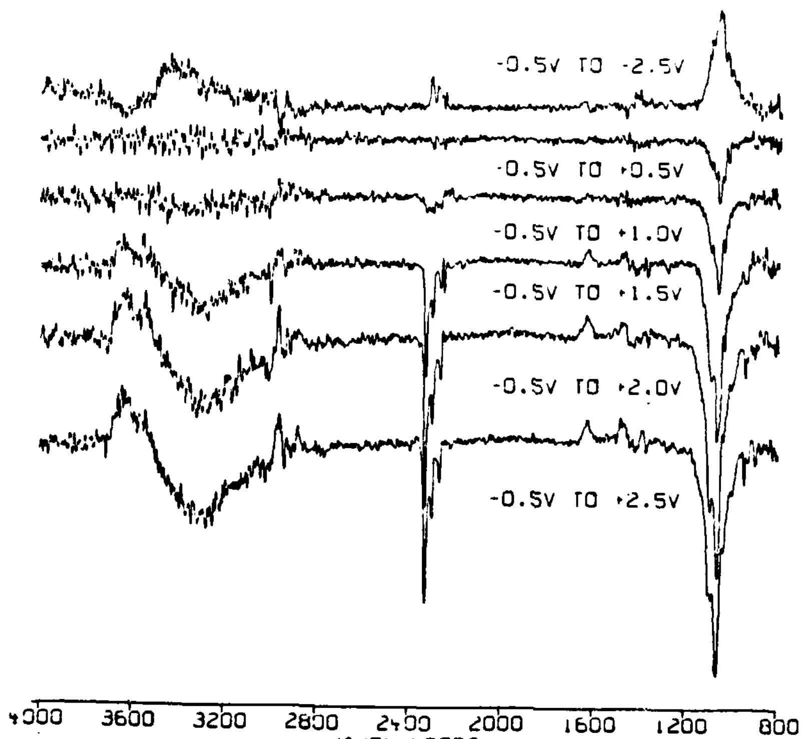
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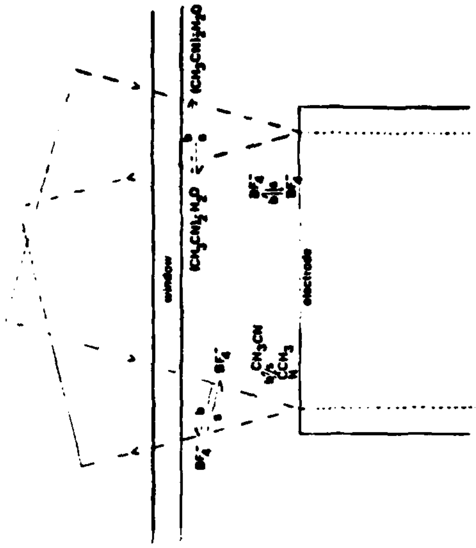

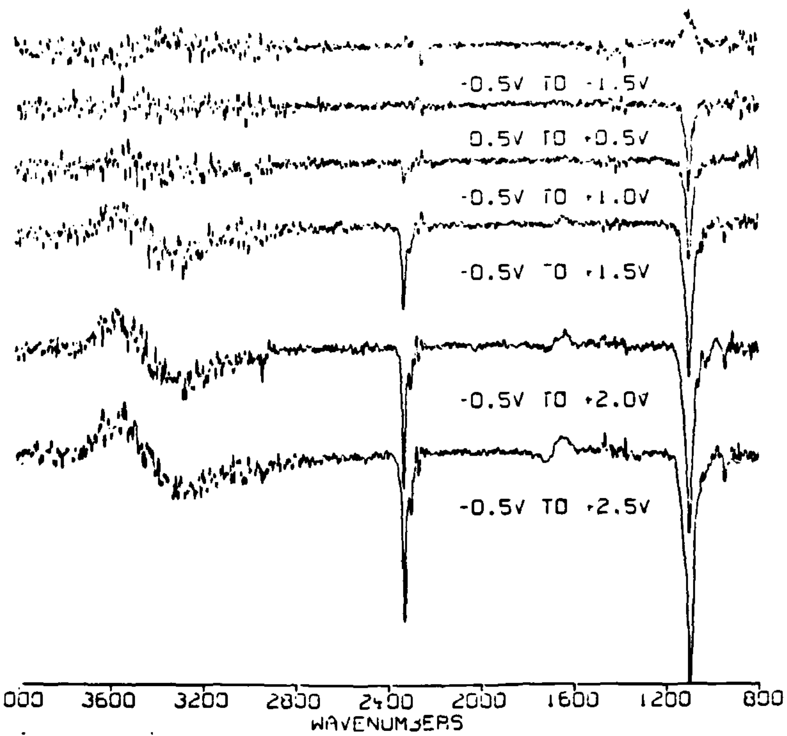
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